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(71) Applicant: HERCULES INCORPORATED
910 Market Street
Wilmington Delaware 19899(US)

(72) Inventor: Cartwright, Richard Vance
R.D.4, Box 93B Coykendall Road
Sussex New Jersey(US)

(72) Inventor: Lees, Ronald Douglas
Rt.1, 379 DD
Bartlesville Oklahoma 74003(US)

(74) Representative: Brock, Peter William et al,
Michael Burnside & Partners 2 Serjeants' Inn Fleet Street
London EC4Y 1HL(GB)

(54) **Gelatinized highly explosive composition and method of preparation.**

(57) The gelatinization by nitrocellulose of an explosive sensitizer composition comprising from 5 to 95% of a liquid nitrated polyol derived from an aliphatic polyol having from 2 to 6 alcoholic hydroxyl groups and from 2 to 10 carbon atoms and from 95 to 5% of metriol trinitrate, (trimethylol ethane trinitrate) is enhanced by a polar compatibility additive selected from dimethylformamide, formamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone and dimethylsulfoxide.

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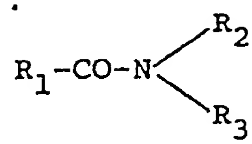
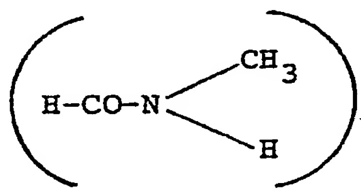
This invention relates generally to the preparation of gelatinized high explosives. It relates particularly to the use of dimethylformamide as a compatibility additive in explosive formulations which include a combination of metriol trinitrate and diethylene glycol dinitrate, as a replacement for nitroglycerine.

Gelation of nitroglycerine by nitrocellulose is easily accomplished and has long been standard practice in dynamite manufacture. However, it is desirable to replace nitroglycerine in dynamite with another component because of the notorious ability of nitroglycerine to produce headaches. A mixture of metriol trinitrate and diethylene glycol dinitrate has been found to be a very promising replacement for nitroglycerine in terms of ease of production, explosive performance and cost. U.S. Patent 3,423,256 discloses an explosive sensitizer composition wherein trimethylolethane trinitrate decreases the impact-sensitivity of the composition as compared to use of the liquid nitrated polyol alone while not decreasing the detonator sensitivity. However, gelation of the combination of metriol trinitrate and diethylene glycol dinitrate by nitrocellulose does not proceed at an acceptable rate under reasonable conditions of dynamite manufacture. U.S. Patent 2,159,973 discloses a process for adding an amide, preferably dimethylformamide, to an organic nitrate to accelerate gelatinization. This reference discloses as organic nitrates the use of nitroglycerine and tetranitroglycerine. This patent discloses the acceleration of gelatinization by incorporating with the nitroglycerin an acid amide of a monobasic fatty acid or an alkyl derivative thereof. The acid amide disclosed has

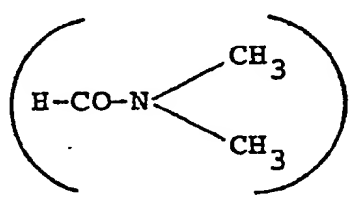
the formula



in which R_1, R_2, and R_3 consist either of hydrogen or an alkyl radical. For example, formamide and its alkyl derivatives are known to be desirable accelerants, in which case, R_1, represents hydrogen. When R_1 represents a CH_3 group the accelerant will be acetamide or an alkyl derivative thereof. R_2 and R_3, likewise, may represent either hydrogen or alkyl groups. Examples of compounds known to be advantageous for use as gelatinization accelerants include formamide ($H-CO-NH_2$), acetamide ($CH_3-CO-NH_2$), monomethylformamide



dimethylformamide



dimethylacetamide ($CH_3-CO-N-(CH_3)_2$), diacetamide ($(CH_3-CO)_2-NH$), propionamide, butylamide, and many others. From this group, dimethylformamide is the preferred gelatinization accelerant.

Gelation of the nitrate ester in dynamite type formulation has a twofold purpose. First, the gel forms a hydrophobic protective coating on water sensitive solids such as ammonium nitrate and sodium nitrate. This coating effect is essential for imparting the water resistance which is needed in wet environments. Secondly, gelation is necessary to prevent separation of the liquid nitrate ester from the rest of the explosive. Separation would greatly reduce the explosive

performance and could possibly produce a serious handling hazard because of contamination of the packaging material by the nitrate ester.

This invention includes adding between 0.05% and 0.20%, based on the overall formulation, of N,N-dimethylformamide as a polar compatibility additive to a mixture of metriol trinitrate and diethylene glycol dinitrate, which is included for explosive sensitization of a non-nitroglycerine dynamite-type explosive formulation. The resulting product has improved consistency and superior water resistance.

In the process of this invention, between 0.05% and 0.20% dimethylformamide is required for dependable enhancement of gelation. Amounts of dimethylformamide in excess of 0.20% would not significantly improve gelation. In fact, amounts in excess of 0.20% would make water resistance worse because of the hydrophilic nature of dimethylformamide. Other polar additives can be used in place of dimethylformamide including formamide, N,N-dimethylacetamide, N-methyl 2-pyrrolidone, and dimethylsulfoxide.

In the composition of this invention, since the metriol trinitrate is more impact sensitive than diethylene glycol dinitrate, the addition of diethylene glycol dinitrate actually lowers the overall impact sensitivity as compared to the disclosure of U.S. Patent 3,423,256, wherein the metriol trinitrate lessens the shock sensitivity of the nitrated polyol. The metriol trinitrate and diethylene glycol dinitrate can be present in ratios between about 95:5 and 5:95. Preferably the ratio should be between about 40:60 and 60:40. More preferably, the metriol trinitrate and the diethylene glycol dinitrate are present in a ratio of about 50:50.

In the process of this invention, for best results, the nitrate esters, dimethylformamide and nitrocellulose should first be premixed separately from the other solid ingredients.

Although there are a number of nitrocellulose solvents, such as acetone and ethyl acetate, which can be added to a mixture of nitrocellulose and nitrate esters to induce gelation, these solvents are not included in the present inven-

tion. The quantities required would be high enough to result in a decrease in the explosive sensitivity of the dynamite to an unacceptably low level. The process of this invention will allow dynamite-type formulations which do not contain nitroglycerine, to be kept under water or in a wet environment between 2 and 20 times longer than dynamite-type formulations which do contain nitroglycerine.

The following examples, in the opinion of the inventors, represent preferred embodiments of this invention.

Examples 1-3

The amounts of ingredients used in these examples are based on the production of 5000 gram experimental batches. 500 grams each of metriol trinitrate and diethylene glycol dinitrate were first mixed with 25 grams of dynamite-grade nitrocellulose and the amount of dimethylformamide shown in Table I, below, for 5 minutes. The following dry ingredients were mixed together in a separate container: 1,239.5 grams of sodium nitrate, screened through a six mesh screen (3.33 mm. opening); 143 grams balsa dust; 143 grams tamarind seed flour; 21.5 grams powdered chalk; and the amount of ammonium nitrate shown in Table I after being passed through a 10 mesh screen (1.7 mm. opening). In the process of this invention, the liquid and dry ingredients were then mixed together for approximately 5 minutes. The mixtures were then packed into waxed paper shells, 203.2 mm. in length and having a diameter of 31.75 mm.

The water resistance of the product was determined by finding the maximum length of time that a cartridge could be kept under 3.5 m. of water and still be detonated by a number 6 blasting cap. The results of those tests are shown in Table I.

TABLE I

EXAMPLE NO.	DIMETHYLFORMAMIDE, GRAMS	DIMETHYLFORMAMIDE, PERCENT	AMMONIUM NITRATE GRAMS	LONGEST TIME FOR DETONATION, HOURS	SHORTEST TIME FOR FAILURE, HOURS
CONTROL	0	0	2428	1*	6
1	2.5	.05	2425.5	24	48
2	5.0	.10	2423	72	96
3	7.5	.15	2420.5	96	120*

*Estimate

These results show the effect of dimethylformamide as a compatibility additive in improving the water resistance of the formulations shown in Table I.

Examples 4-7

A series of experiments were conducted which disclosed an improvement in semi-gelatin consistency with increasing use of dimethylformamide. A series of four 7,000 gram mixtures were prepared, each mixture containing equal amounts of diethylene glycol dinitrate and metriol trinitrate. In addition, 0.3% dynamite-grade nitrocellulose, 50% ammonium nitrate, screened through a 24 mesh screen (0.7 mm opening), 16.2% sodium nitrate screened through a 10 mesh screen (1.7 mm opening), 0.5% wood flour, 1.5% balsa dust, 2% tamarind flour, 10% sodium chloride, 0.5% powdered chalk, and 1.0% Alcoa 1651 aluminum was used. The amount of dimethylformamide in each test is shown in Table 2.

The nitrate esters and dimethylformamide were first combined, and then nitrocellulose was then added and mixed for five minutes. The solid ingredients, with the exception of aluminum, were added slowly while stirring. The aluminum was then added and combined throughly by mixing for three minutes. The formulation was then packed into paper shells, each having a diameter of 31.75 mm.

Each cartridge shell was then unrolled, and a 76.2 mm length of the explosive material was cut. In the test, one end of each 76.2 mm stick of explosive was pushed against a hard surface until it assumed the shape of a mushroom. It was

then inverted. If the mushroom disintegrated, the semi-gelatin quality was considered to be poor. Semi-gelatin quality was considered to be good if the integrity of the mushroom shape is maintained.

The results which were obtained are shown in Table II.

TABLE II

EXAMPLE NO.	METRIOL TRINITRATE %	DIETHYLENE GLYCOL DINITRATE %	DIMETHYL-FORMAMIDE %	SEMI-GELATIN QUALITY
CONTROL	9	9	0	Poor
4	8.975	8.975	0.05	Fair
5	8.950	8.950	0.10	Good
6	8.900	8.900	0.20	Good

These results demonstrate that the addition of dimethylformamide improves the consistency of the packed material. In turn, good consistency usually results in enhanced water resistance.

Gelation of a liquid polymer requires substantial polymer-solvent interaction. The polymer and solvent interact well if their polarities are well matched. It is believed that nitroglycerine and nitrocellulose have comparable polarities while the metriol trinitrate/diethylene glycol dinitrate mixture is appreciably less polar than nitrocellulose. However, dimethylformamide is a highly polar solvent as well as a solvent for nitrocellulose. Therefore, the addition of dimethylformamide to the metriol trinitrate/diethylene glycol dinitrate mixture can increase its overall average polarity to a point where it is comparable to that of nitrocellulose. In effect, the addition of dimethylformamide increases the affinity of nitrocellulose for the metriol trinitrate/diethylene glycol dinitrate combination and performs as a compatibility additive for these two constituents.

Dynamite-type formulations manufactured by the process of this invention are expected to have significant utility as a

substitute for conventional dynamite, i.e., in mining, tunneling, ditching, construction, seismic exploration and other applications.

CLAIMS:

1. A high explosive composition comprising: an explosive sensitizer composition consisting essentially of from 5 to 95% of a liquid nitrated polyol derived from an aliphatic polyol having from 2 to 6 alcoholic hydroxyl groups and from 2 to 10 carbon atoms, and from 95 to 5% of metriol trinitrate (trimethylol ethane trinitrate), said sensitizer composition gelatinized by nitrocellulose, characterized in that said composition includes a polar compatibility additive selected from dimethylformamide, formamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone and dimethylsulfoxide.

2. An explosive composition in accordance with Claim 1 characterized by including in addition an inorganic oxidizer salt.

3. An explosive composition in accordance with Claim 1 or 2 characterized in that said nitrated polyol is diethylene glycol dinitrate and said diethylene glycol dinitrate and said metriol trinitrate are present in a ratio of between 60:40 and 40:60.

4. An explosive composition in accordance with any of Claims 1 to 3 characterized in that the polar compatibility additive is dimethylformamide in an amount between 0.05 and 0.20% of said explosive composition.

5. A process of enhancing compatability between nitrocellulose and a combination of metriol trinitrate (trimethylol ethane trinitrate) and diethylene glycol dinitrate, characterized by adding a polar compatibility additive selected from dimethylformamide, formamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone and dimethylsulfoxide.

6. A process in accordance with Claim 5 characterized in that said compatibility additive is dimethylformamide.

7. A process in accordance with Claim 6 characterized in that said dimethylformamide is added in an amount between 0.05 and 0.20%.